

Atomic Motions in Confined Polymer Films

Material properties at surfaces and interfaces often deviate from their bulk values. An example is viscoelastic properties that are important in many applications such as chemically amplified photoresists, lubricants, adhesives, etc. A viscosity increase of a liquid polymeric film, like those used for hard disc lubricants, could have deleterious consequences. Likewise, a viscosity decrease in a thin photoresist film could enhance photoacid diffusion and create image blur. It is clearly important to characterize the molecular level mobility in thin polymer films. Of particular interest are changes in the glass transition temperature T_g , since the glass transition corresponds to a sharp change in viscosity.

It is well known that atomic thermal motions lead to a decrease in the intensity of the elastically scattered neutrons. In a harmonic solid the intensity is related to the amplitude of the motion through the Debye-Waller factor, $I_{\text{inc}}(Q) \sim \exp(-\frac{1}{3}Q^2\langle u^2 \rangle)$, where Q is the scattering vector and $\langle u^2 \rangle$ is the mean-square atomic displacement. In a logarithmic plot of I_{inc} as a function of Q^2 , $\langle u^2 \rangle$ is proportional to the slope of a linear fit to the data. This approximation has proven very useful in studying the dynamics of polymers, both synthetic [1] and biological [2], despite the fact that their atomic motions are typically anharmonic.

The elastic incoherent neutron scattering intensities can be measured as a function of temperature on the NCNR's High Flux Backscattering Spectrometer (HFBS), using the "Fixed Window" mode. Polycarbonate (PC) films, seen in Fig. 1, are spin cast onto Si wafers, sectioned into small rectangles, and stacked into an Al sample cell. The scattering from the Si substrates and Al cell are negligible because their Bragg peaks are beyond the Q range of the instrument ($0.25 \text{ \AA}^{-1} < Q < 1.75 \text{ \AA}^{-1}$); the scattering is dominated by the large incoherent cross-section of the amorphous PC.

Ideally there should be 200 mg of PC per cell to maximize the signal and minimize multiple scattering effects (90 % transmission). For the Si-supported films we are limited by 0.5 mg to 10 mg of PC per cell and thus obtain a very weak signal (99 % transmission). However, the HFBS is sufficiently sensitive to observe this signal, as seen in Fig. 2 where the temperature dependence of the elastic scattering is shown. The relative magnitude of the intensity

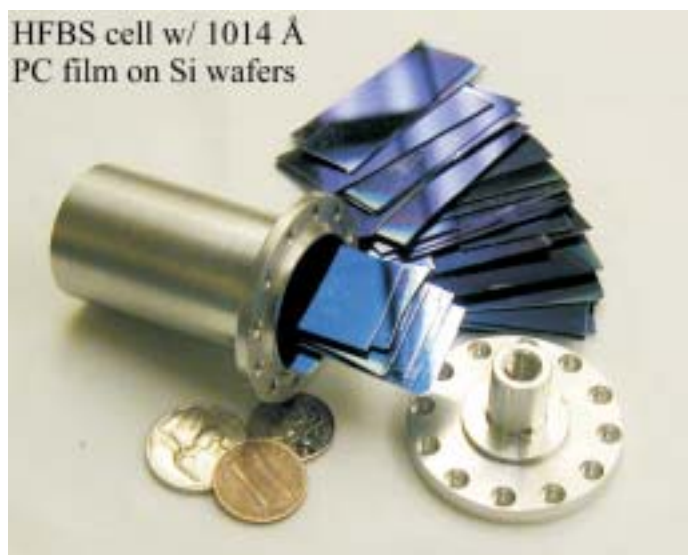


FIGURE 1. A stack of 1014 Å PC films (notice the blue tint) on thin slabs of Si ready to go into the HFBS spectrometer.

change diminishes with decreasing film thickness, a clear indication of reduced atomic mobility in the thin PC films. Given the HFBS energy resolution of $0.85 \text{ } \mu\text{eV}$, these intensity changes reflect changes in atomic motions at frequencies of 200 MHz or faster.

This reduced mobility is qualitatively reflected in Fig. 3 as strong suppression of $\langle u^2 \rangle$. We emphasize qualitatively because $\langle u^2 \rangle$ arises from a harmonic approximation. Nevertheless, there is a clear reduction in the amplitudes of the thermal motions, both above and below the calorimetric T_g , as the film thickness approaches the root-mean-square (rms) end-to-end length of PC ($R_{\text{ee}} = 160 \text{ \AA}$).

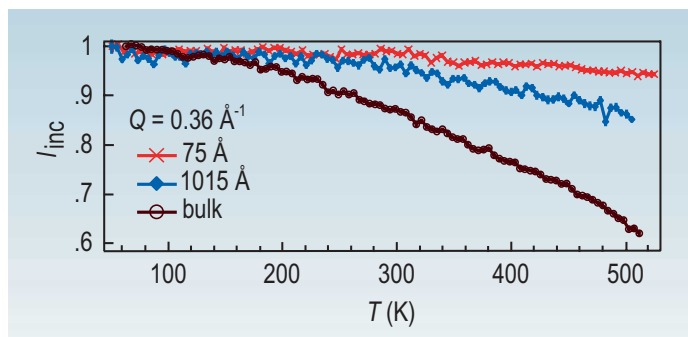


FIGURE 2. The normalized elastic intensities in the HFBS detector at $Q = 0.36 \text{ \AA}^{-1}$. The decrease in intensity at high temperatures reflects the presence of atomic motion in the thin polymer films.

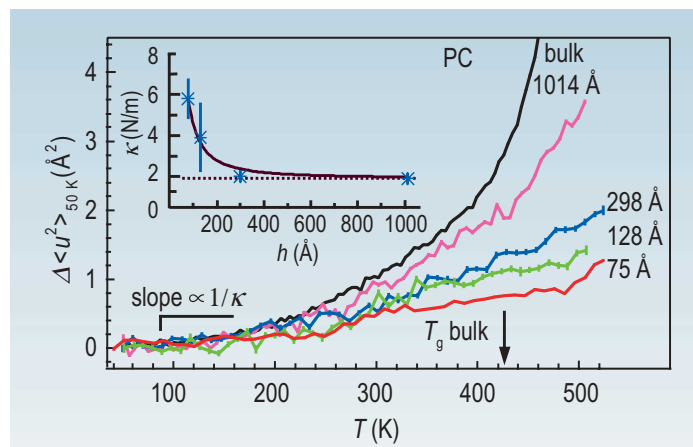


FIGURE 3. $\langle u^2 \rangle$ as a function of temperature for the PC thin films. The inset reveals a stiffening of the harmonic (low temperature) force constant κ with decreasing film thickness h .

At temperatures below 200 K, $\langle u^2 \rangle$ is small and the harmonic approximation is reasonable. In this regime the inverse of the slope of $\langle u^2 \rangle$ vs. T is proportional to an elastic force constant κ . The inset of Fig. 3 displays a dramatic stiffening of κ with confinement. This implies that the atoms or molecules in PC become strongly caged by their environment in the thinner films.

Similar $\langle u^2 \rangle$ measurements on thin films of polymethyl methacrylate (PMMA; $R_{ee} = 915$ Å) and polyvinyl chloride (PVC; $R_{ee} = 437$ Å) are shown in Figs. 4(a) and 4(b). There is a suppression of $\langle u^2 \rangle$ with decreasing film thickness above the bulk T_g that is qualitatively consistent with the PC films. However, below the T_g for bulk PMMA the suppression is less pronounced, and not observed in the PVC films. Careful inspection of Figs. 3 and 4 suggests a relation between the magnitude of $\langle u^2 \rangle$ at T_g in the bulk and the degree of $\langle u^2 \rangle$ suppression in the thin glassy films.

Bulk PC has the largest $\langle u^2 \rangle$ at T_g , indicating extensive mobility. In fact, PC is well known for its segmental mobility in the glassy state, which is in part related to its superior impact resistance. Molecular mobility helps dissipate strain energy. (PC is used in bullet-proof glass.) This extensive mobility is also susceptible to thin film confinement, as also seen through the stiffening of the elastic constants from 1.9 N/m in bulk PC to 5.8 N/m in the 75 Å film. At the other extreme, bulk PVC has the smallest $\langle u^2 \rangle$ at T_g , indicating a lack of motions to be affected by confinement. This is also consistent with the strong intermolecular

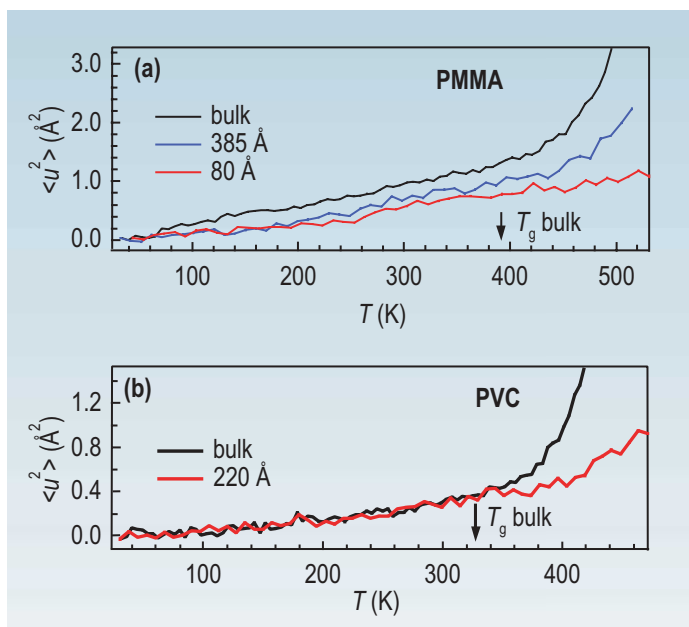


FIGURE 4. $\langle u^2 \rangle$ as a function of thickness and temperature for similar PMMA (a) and PVC (b) films.

caging at low temperatures; both bulk PVC and the 220 Å film have large elastic force constants of 4.6 N/m. This lack of mobility reflects the observation that PVC is a brittle polymer that needs high levels of plasticization for practical use. Only when PVC is taken above the bulk T_g , where long-range motions dominate, do the effects of confinement become evident.

In short, we have seen two different responses to thin film confinement. While there is a general suppression of $\langle u^2 \rangle$ and the fast dynamics, polymers with greater mobility are more susceptible to confinement, especially below the calorimetric T_g . In contrast, polymers with strongly localized motions appear bulk-like, even in highly confined glassy films. More details of these studies can be found in our upcoming publications [3–5].

References

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